Intramolecular Photocycloaddition of *N*-Alkenyl Substituted Maleimides: A Potential Tool for the Rapid Construction of Perhydroazaazulene Alkaloids

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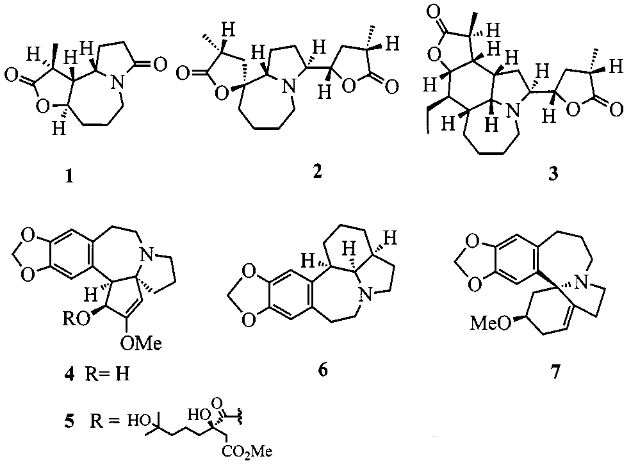
UV irradiation of a number of *N*-alkenyl-substituted maleimide derivatives leads to the formation of complex perhydroazaazulenes in excellent yields. The overall process can be considered as a formal intramolecular [5+2] cycloaddition. Substrates were prepared by Mitsunobu coupling of the appropriate alkenols with various maleimides. Methyl substitution of the alkenyl side chain gave the cycloadducts **13a–g** in good yields, with moderate to high stereoselectivity being observed for **13e** and **13g**, respectively. Use of cyclic alkene side chains led to the formation of tri- and tetracyclic products with high degrees of stereoselectivity in most cases. Some of the polycyclic ring systems that were prepared constitute the core skeleton of a number of complex alkaloids. The substrate **29** underwent an unexpected [2+2] photocycloaddition to yield the unusual cyclobutane **31**.

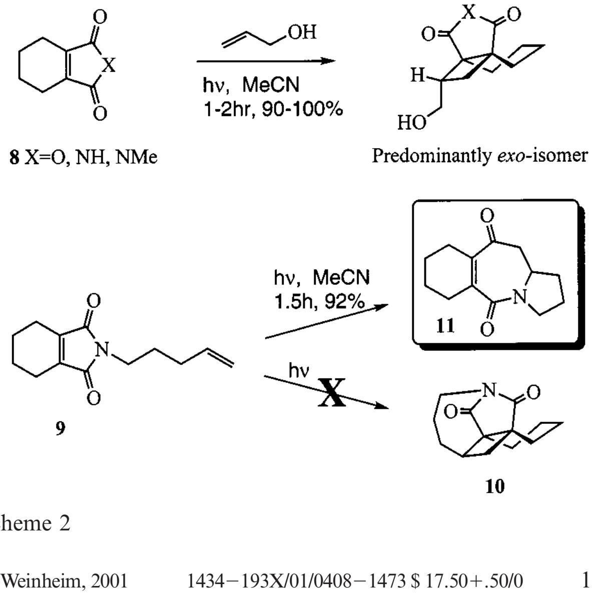
Introduction

The perhydroazaazulene ring system is a very common structural motif in nature and is present in a large variety of structurally diverse alkaloids, a number of which are shown in Scheme 1. For example, stemoamide **1**, croomine **2** and neotuberostemonine **3** are amongst a number of alkaloids found in the roots of *Stemona*, extracts of which have been used in traditional Chinese medicine for the treatment of respiratory disorders such as bronchitis and tuberculosis.[1] Other important alkaloids include cephalotaxine **4** and homoharringtonine **5**; the latter shows promise as a treatment for chronic myelogenous leukemia.[2] Hexahydroapoerysopine **6** has been the focus of a number of studies as it is formed from a rather unusual "apo" rearrangement of the naturally occurring alkaloid erysopine.[3] Finally, robustidine **7**, isolated from the leaves of *P. brachyphylla*, is one of a number of homoerythrinan alkaloids which contain the perhydroazaazulene system spiro fused to a cyclohexene ring.[4]



Scheme 1

For a number of years we have been studying the intermolecular [2+2] photocycloaddition reactions of tetrahydrophthalic anhydride **8** (X = O) and the corresponding imide **8** (X = NH, NMe) with alkenol and alkynol derivatives.[5] These reactions have proved to be extremely efficient, with the resulting cycloadducts being obtained in high yields and excellent stereoselectivity. On attempting to explore the intramolecular [2+2] photocycloaddition of the pentenyl-substituted imide **9** to the cyclobutane **10** we were somewhat surprised to observe the rapid and exclusive



Scheme 2

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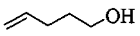
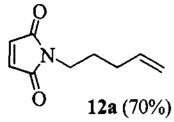
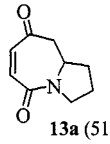
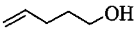
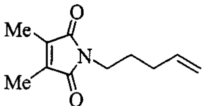
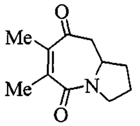
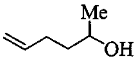
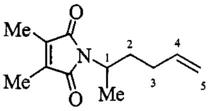
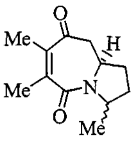
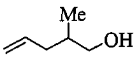
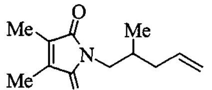
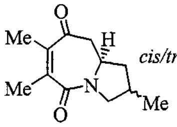
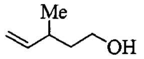
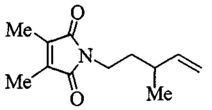
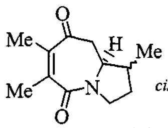
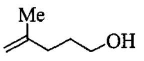
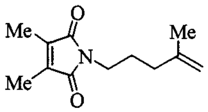
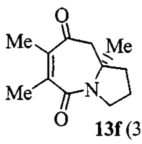
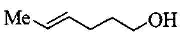
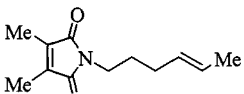
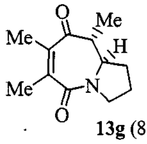
formation of the tricyclic azepine **11** in excellent yield. Independent studies by the groups of Mazzocchi[6] and Maruyama and Kubo[7] have previously demonstrated that *N*-substituted phthalimides undergo similar inter- and intramolecular cycloadditions with alkenes. After detailed studies a plausible mechanism for this unusual mode of cycloaddition was proposed by Mazzocchi.[6] The conversion of **9**→**11** (Scheme 2) is the first example of this formal [5+2] cycloaddition reaction with non-aryl imides and holds great promise as a powerful tool in the rapid construction of complex perhydroazaazulenes. In this paper we describe our full experimental details[8] on the scope and limitations of the intramolecular photocycloaddition of unsaturated imides which we intend to use as a key step in the synthesis of the alkaloids **1**−**7**.

Results and Discussion

Acyclic Alkene-Maleimide Photocycloadditions

Table 1 shows the intramolecular photocycloaddition of a number of substituted maleimide derivatives. The cycloaddition precursors could be readily assembled with a maleimide-alkenol Mitsunobu coupling procedure, in moderate to high yields, on a multigram scale. Irradiation of the parent imide **12a** (Entry 1) showed complete disappearance of

Table 1. Acyclic alkene-maleimide photocycloaddition

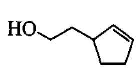
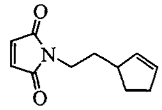
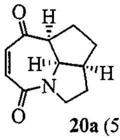
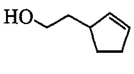
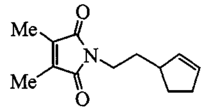
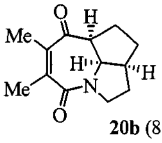
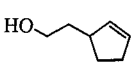
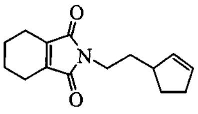
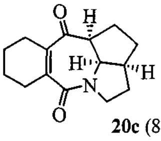
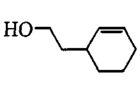
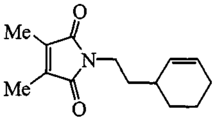
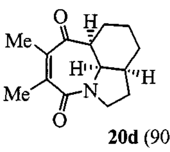
Entry	Alkenol	Mitsunobu Product (% yield)	Photocycloadduct (% yield)
1		 **12a** (70%)	 **13a** (51%)
2		 **12b** (67%)	 **13b** (99%)
3		 **12c** (50%)	 *cis/trans* 1.27:1 **13c** (69%)
4		 **12d** (72%)	 *cis/trans* 1:1 **13d** (87%)
5		 **12e** (81%)	 *cis/trans* 3:1 **13e** (90%)
6		 **12f** (79%)	 **13f** (33%)
7		 **12g** (97%)	 **13g** (88%)

the starting material after 2 h, to give a product that appeared to be a [2+2] heterodimer[9] of the expected cycloadduct **13a** with the starting material **12a**. When **12a** was irradiated for shorter periods of time it was possible to isolate the desired [5+2] cycloadduct **13a** and unchanged starting material in reasonably good yields. Irradiation of the dimethyl imide **12b** (Entry 2) gave an excellent yield of the desired cycloadduct **13b** without any dimerisation of the product, even after prolonged reaction times. This result proves that substitution of the imide alkene effectively slows down dimerisation thus maximising the yield of the primary photocycloadduct. We then performed a study to assess the stereochemical influence that a methyl group would have on the cycloaddition when placed at all possible positions of the 5-carbon alkene unit. Methyl substitution at C1 (Entry 3) gave a very slight excess of one diastereomer over the other (12% *de*) but unfortunately it was not possible to separate these or prove which isomer predominated. Substitution at C2 (Entry 4) gave no observed selectivity and an inseparable 1:1 mixture of diastereomers was obtained. More significantly, substitution at C3 (Entry 5) gave a mixture of diastereomers in a 3:1 ratio. Although it was not possible to separate these, the relative stereochemistry of the major isomer (**13e**) was shown, by careful NOE studies, to be *cis*. These results suggest that substitution at C1 and C3 with groups more sterically demanding than methyl should lead to greater levels of diastereoselectivity. Although substitution at C4 (Entry 6) could only give one isomer, the methyl group had a negative effect on the rate of photocycloaddition and unchanged starting material still remained even after 24 h of irradiation. Significantly, substitution at C5 (Entry 7) led to a single diastereoisomer of the cycloadduct whereby the geometry of the alkene had been retained. This result, along with Entry 5, yields important information on the nature of the mechanism of this reaction (vide infra).

Mechanism

Although the mechanism is not known with certainty it can be postulated from the work of Mazzocchi[6] that the reaction proceeds by a direct [2+2] cycloaddition onto the excited amide resonance structure **14** to give the zwitterionic tricyclic species **15**, which then undergoes a spontaneous fragmentation to the product (Scheme 3). The fact that the alkene geometry is retained with the C5-substituted example (Table 1, Entry 7) would certainly support this type of mechanism — if a stepwise cycloaddition process was operating it would be expected that bond rotations in the resulting intermediates would lead to epimeric products. Furthermore, these cycloadditions must be remarkably fast, given that we have found that the intermolecular [2+2] photocycloaddition of the maleimide alkene with other alkenes is a very facile and efficient process.[5] Although it is probably mechanistically incorrect we have found it very useful, for retrosynthetic purposes, to consider this reaction as a diradical [5+2] cycloaddition as illustrated below. Furthermore, for Entry 5 it is possible to consider the transition state **16** in which the alkenyl side chain adopts a conformation where the C3 methyl group is equatorial. Use of this model successfully predicts the observed stereochemistry of

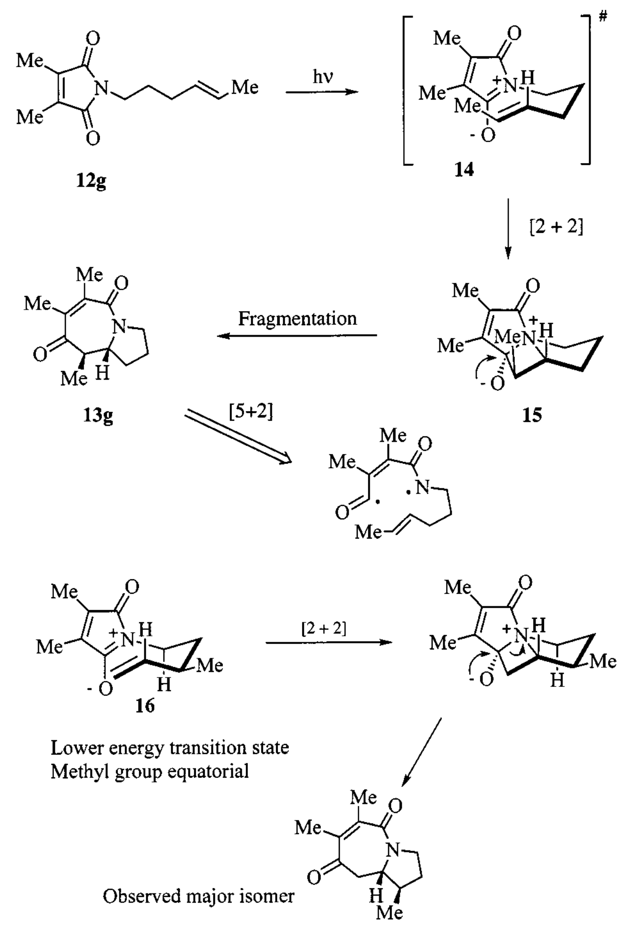
Table 2. Cyclic alkene-maleimide photocycloaddition

Entry	Alkenol	Mitsunobu Product (% yield)	Photocycloadduct (% yield)
1	 **17**	 **19a** (70%)	 **20a** (50%)
2		 **19b** (66%)	 **20b** (83%)
3		 **19c** (64%)	 **20c** (89%)
4	 **18**	 **19d** (68%)	 **20d** (90%)

the obtained major (*cis*) isomer of **13e**, and thus lends further weight to the mechanism proposed.

Cyclic Alkene-Maleimide Photocycloadditions

We then turned our attention to the investigation of more complex alkene systems with a view to testing the limits of the photocycloaddition and thus evaluating its potential in alkaloid synthesis. We had at hand the cyclic alkenols **17**[10] and **18**[11] which underwent successful Mitsunobu coupling with a number of imides to give the photocycloaddition precursors (Table 2). Irradiation of **19a** for 20 min. gave a 50% isolated yield of the tricyclic azepine **20a** as a single diastereoisomer. Irradiation for >20 min. resulted in a dramatic reduction in the yield of **20a**, which again was presumably being consumed by dimerisation. Photocycloaddition of the dimethyl derivative **19b** (Entry 2) gave an excellent yield of the tricyclic azepine **20b** without any dimerisation. Irradiation of the tetrahydrophthalimide derivative **19c** gave rise to the exclusive formation of the tetracycle **20c** in 89% yield (Entry 3). Irradiation of the cyclohexenyl-derived imide **19d** (Entry 4) yielded the tricyclic azepine **20d** in excellent yield, thus providing a successful model study for the synthesis of hexahydroapoerysopine **6**. The fact that a complex tetracyclic product such as **20c** can be formed efficiently and stereoselectively in just two steps from readily available starting materials illustrates the great potential of this photocycloaddition. The stereochemistry observed in these cycloadditions was confirmed by NOE studies (Figure 1) and is consistent with the proposed mechanism (Scheme 3).



Lower energy transition state
Methyl group equatorial

Observed major isomer

Scheme 3

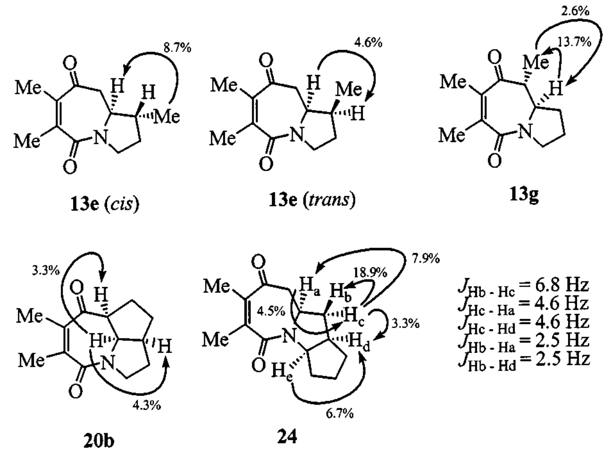
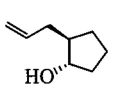
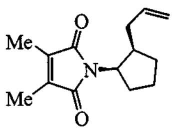
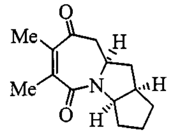
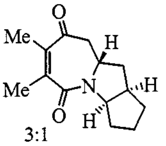
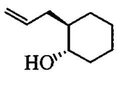
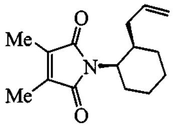
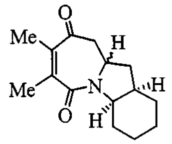
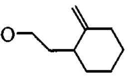
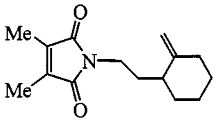
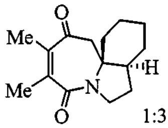
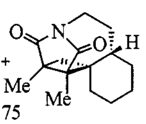


Figure 1. Selected NOE results and H-H coupling constants

Miscellaneous Alkene-Maleimide Photocycloadditions

Table 3 shows a number of other maleimide systems that were investigated during the course of this study. In Entries 1 and 2 we elected to study the stereochemical effect of placing the alkene side chain on a carbocyclic ring adjacent to a maleimide unit. The *trans* alkenols **21**[12] and **22**[13] were prepared by literature methods and underwent Mitsunobu coupling with dimethylmaleimide to yield the *cis* photocycloaddition precursors **23** and **26** respectively. Although photocycloaddition was clean and high yielding in both cases, the levels of diastereoselectivity observed were rather mixed. Only the cyclopentane derivative **23** showed any levels of selection with the *cis* isomer **24** being formed as the major product (3:1). The relative stereochemistry of the *cis* isomer was assigned by a combination of NOE experiments and coupling constants (Figure 1). It is possible that the larger cyclohexyl ring allows a greater degree of conformational flexibility during cycloaddition which in turn means that there is little energy difference between the two transition states leading to the *cis* and *trans* isomers of **27**. As part of a model study towards homoerythrinan alkaloids such as robustidine **7**, the maleimide **29** (Entry 3) was prepared by Mitsunobu coupling to the known exocyclic alkenol **28**.[14] Irradiation of this compound led to a rather interesting, and totally unexpected, result. Although the formal [5+2] cycloadduct **30** was formed the major cycloadduct was the intramolecular [2+2] photocycloadduct **31**. Definitive proof of this structure was obtained by X-ray crystallography (Figure 2). This was a very surprising result as it had not been observed in any of the previous examples; indeed it was rather ironic since this was the very result we expected from the initial cycloaddition studies of **9**! It is likely that due to the connectivity of the maleimide **29** the transition state leading to [5+2] cycloaddition onto the ex-

Table 3. Miscellaneous alkene-maleimide photocycloadditions

Entry	Alkenol	Mitsunobu Product (% yield)	Photocycloadduct (% yield)
1	 **21**	 **23** (65%)	 3:1  **24** (63%) **25** (20%)
2	 **22**	 **26** (62%)	 1:1 **27** (90%)
3	HO  **28**	 **29** (69%)	 + 1:3.75  **30** (20%) **31** (75%)

ocyclic double bond is less favourable and, in this particular case, [2+2] cycloaddition is preferred. Further studies with substituted derivatives as well as molecular modelling will be necessary to elucidate the factors that control this fascinating switch in the mode of cycloaddition and thus tune the reaction in favour of the robustidine skeleton.

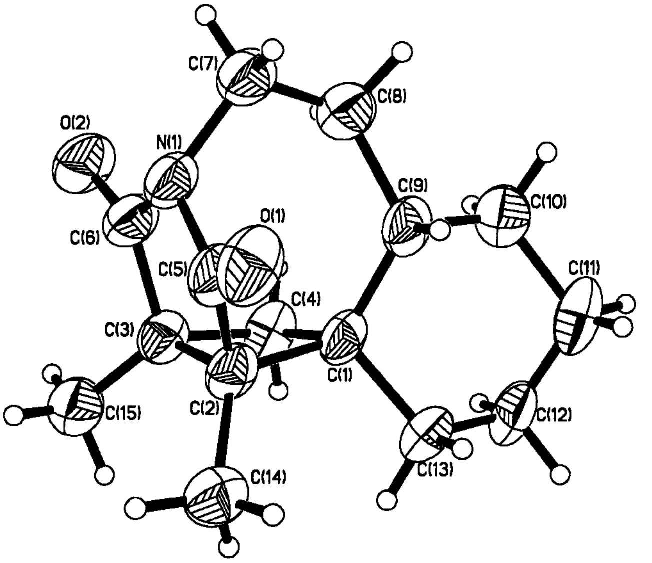
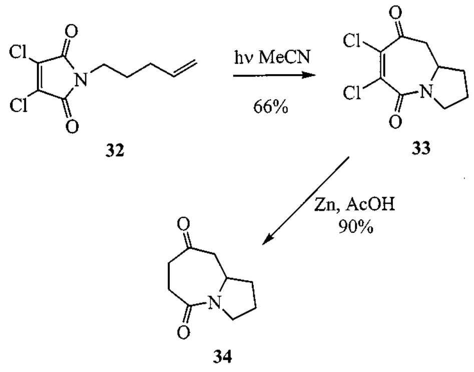


Figure 2. Molecular structure of **31** with 50% thermal ellipsoids; selected bond lengths (Å): C(1)−C(2) 1.615(10), C(2)−C(5) 1.484(11), C(2)−C(3) 1.565(10), C(3)−C(6) 1.501(11), C(3)−C(4) 1.569(11), C(5)−O(1) 1.198(9), C(5)−N(1) 1.412(10), C(6)−O(2) 1.221(10), C(6)−N(1) 1.394(10), N(1)−C(7) 1.470(10)

As discussed in Table 1, irradiation of the parent maleimide **12a** (Entry 1) led to problems which were thought to be a result of dimerisation of the product. This problem was overcome by the use of dimethyl maleimide, which prevents dimerisation presumably due to the steric hindrance afforded by the two methyl groups. However, this ultimately imposes a severe constraint on the use of the resulting photoadducts in alkaloid synthesis, namely an intractable problem associated with removal of the dimethyl groups. A solution to this presented itself with the synthesis of the dichloroimide **32** which underwent photocycloaddition, without any observed dimerisation, to afford the dichloroazepine **33** in 66% yield. Treatment of this with Zn/AcOH affords the reduced/dechlorinated product **34** in excellent yield (Scheme 4). Present work is concerned with evaluating the dichloromaleimide unit in alkaloid synthesis as well as with studies using other removable blocking groups such as strategies employing mono-bromo and mono-trimethylsilyl-substituted maleimides.

Conclusion

The photochemical formal [5+2] cycloaddition of 4-alkenyl-substituted maleimide derivatives has proved to be a remarkable process for the formation of fused azepine ring systems. The reaction works efficiently with both simple as well as more elaborate 4-alkenyl subunits and yields a number of ring systems in good yield, in only two steps, from simple starting materials. Significant degrees of stereoselectivity are observed with methyl substitution of the alkenyl



Scheme 4

side chain, especially at positions C3 and C5. Use of cyclic alkenes results in the synthesis of complex polycyclic azepines with high levels of diastereoselection. We believe that this will have wide application in the synthesis of the azepine based alkaloids shown in Scheme 1 and we will report progress in this area in due course.

Experimental Section

General: The UV source used in this study was a water cooled, 125 W medium pressure mercury discharge lamp with a 30 mm arc length. These lamps were obtained from 125 W Osram HQL (MBF-U) bulbs by puncturing the outer glass envelope with a heated glass rod and removing the mercury lamp from inside by cutting the two copper electrodes as close to the screw thread as possible. These were then used as normal with a standard 125 W power supply obtained from Photochemical Reactors Ltd, Reading. NMR spectra were obtained in deuterochloroform (unless otherwise stated), with chemical shifts measured downfield from TMS (^1H) or referenced to the residual solvent resonance (^{13}C) using Joel JNM-6X 270, Joel JNM − 300 and Varian Unity 300 spectrometers. Infrared spectra were recorded on a Perkin−Elmer 1720 X FT spectrometer using sodium chloride plates. Low resolution, electron impact mass spectra were run on a Kratos MS25 or a Fisons Autospec. Elemental microanalyses were carried out on a Carlo Erba EA 1108. High resolution mass spectra were run at the EPSRC Mass Spectrometry Service at Swansea or on a Micromass autospec at Bristol. Flash chromatography was carried out using Merck silica 60 (40−63 μm) eluting with the solvents stated. TLC analyses were performed using Camlab polygram® SIL G/UV$_{254}$ plastic backed plates (0.25 mm layer of silica) and visualised using UV radiation (254 nm), alkaline potassium permanganate(VII) solution or phosphomolybdic acid solution. Melting points were obtained using a Köpfler hot stage apparatus and are uncorrected. Petroleum ether refers to the fraction boiling in the range 40−60 °C.

X-ray Crystallography: Data were collected at 298 K on a Siemens P4 diffractometer using graphite-monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å) and ω-scans, and were corrected for Lorentz polarization, absorption and extinction effects. The structure was solved by direct methods, and refined (anisotropic U for C, N and O atoms, H-atoms in calculated positions) by full-matrix least-squares on F^2 (all data). Crystal data for **31** ($C_{15}H_{21}NO_2$): colourless chunk, 0.30 × 0.30 × 0.10 mm, monoclinic, space group Cc, $a = 13.416(4)$, $b = 13.918(3)$, $c = 7.599(3)$ Å, $\beta = 110.72(3)°$, $V = 1327.1(7)$ Å^3, $\rho_{calcd.} = 1.238$ Mgm^{-3}, μ(Mo-K_α) = 0.081 mm^{-1}, $F(000) = 536$, $4.4 < 2\theta < 50.0°$; 1441 reflections measured, 1323 unique ($R_{int} = 0.1181$), wR_2 (all data) = 0.2437, $S = 1.013$, R_1 [$I > 2\sigma(I)$] = 0.0856, largest diff. peak/hole = 0.312/−0.290 eÅ^{-3}. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as Supplementary Publication no. 149544. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk)

4,5,6,7-Tetrahydro-2-pent-4-enylisoindole-1,3-dione (9): A solution of tetrahydrophthalimide (1 g, 6.62 mmol), in anhydrous DMF (20 mL), was added dropwise to a stirred suspension of NaH (0.4 g, 9.93 mmol, 60% oil dispersion) in anhydrous DMF (20 mL) under nitrogen at 0 °C. The resulting suspension was stirred for 30 min. at 0 °C after which time 5-iodopent-1-ene (1.6 g, 7.95 mmol) in anhydrous DMF (10 mL) was added dropwise. The reaction mixture was allowed to warm to room temperature and then stirred for a further 45 min. after which it was poured onto ice/water (50 mL). The resulting mixture was extracted with EtOAc (200 mL) and the organic layer washed with water (5 × 50 mL), brine (50 mL) and then dried over $MgSO_4$. The solvent was removed in vacuo and the title compound purified by flash chromatography (10% EtOAc/petroleum ether) to give a colourless oil (0.73 g, 50%). − IR (film): $\tilde{\nu} = 1769, 1701, 1641$ cm^{-1}. − ^1H NMR (300 MHz, $CDCl_3$): δ = 5.88−5.73 (m, 1 H), 5.07−4.95 (m, 2 H), 3.49 (t, J = 7.3 Hz, 2 H), 2.35−2.31 (m, 4 H), 2.06 (q, J = 7.3 Hz, 2 H), 1.79−1.61 (m, 6 H). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 171.2 (C=O), 141.3 (C), 137.4 (CH), 115.02 (CH_2), 37.0 (CH_2), 30.9 (CH_2), 27.8 (CH_2), 21.3 (CH_2), 19.9 (CH_2). − $C_{13}H_{17}NO_2$ (219.28): calcd. C 71.19, H 7.82, N 6.39; found C 71.52, H 7.69, N 6.42. − LRMS (EI): m/z = 219 [M$^+$], 191, 164, 152.

General Procedure for the Mitsunobu Reaction: DEAD (1.5 equiv.) was added dropwise to a stirred solution of the imide (1 equiv.), the alcohol (1−1.2 equiv.) and triphenylphosphane (1.5 equiv.) in anhydrous THF (30 mL/equiv.) under nitrogen at 0 °C. The solution was allowed to warm to room temp. and stirred for 24−48 h (TLC control). After this time the reaction was evaporated onto silica gel, and purified by flash chromatography (10−30% ether/petroleum ether).

1-Pent-4-enylpyrrole-2,5-dione (12a): Maleimide (2.49 g, 25.6 mmol) and 4-penten-1-ol (2.0 g, 23.3 mmol) were reacted according to the general Mitsunobu procedure above to give the title product as a clear oil (2.695 g, 70%). − IR (film): $\tilde{\nu} = 2940, 1770, 1700$ cm^{-1}. − ^1H NMR (300 MHz, $CDCl_3$): δ = 6.45 (s, 2 H), 5.73 (ddt, J = 17.1, 10.1, 6.5 Hz, 1 H), 5.02−4.90 (m, 2 H), 3.48 (t, J = 7.5 Hz, 2 H), 2.05−1.97 (m, 2 H), 1.64 (pent., J = 7.5 Hz, 2 H). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.9 (C=O), 137.2 (CH), 134.1 (CH), 115.3 (CH_2), 37.2 (CH_2), 30.7 (CH_2), 27.4 (CH_2). − $C_9H_{11}NO_2$ (165.19): calcd. C 65.45, H 6.67, N 8.48; found C 65.28, H 6.68, N 8.25. − LRMS (EI): m/z = 165 [M$^+$], 110.

3,4-Dimethyl-1-pent-4-enylpyrrole-2,5-dione (12b): Dimethylmaleimide (0.180 g, 1.44 mmol) and 4-penten-1-ol (0.124 g, 1.44 mmol) were reacted according to the general Mitsunobu procedure above to give the title product as an oil (0.187 g, 67%). − IR (film): $\tilde{\nu} = 2930, 1770, 1700, 1640$ cm^{-1}. − ^1H NMR (300 MHz, $CDCl_3$) δ = 5.80−5.41 (m, 1 H), 5.21−4.84 (m, 2 H), 3.49 (t, J = 7.5 Hz, 2 H), 2.12−2.02 (m, 2 H), 1.96 (s, 6 H), 1.67 (pent., J = 7.5 Hz, 2 H). − ^{13}C NMR (75 MHz, $CDCl_3$) δ = 172.3 (C=O), 137.4 (C), 137.0 (CH), 115.1 (CH_2), 37.2 (CH_2), 30.7 (CH_2), 27.5 (CH_2), 8.4 (CH_3). − $C_{11}H_{15}NO_2$ (193.24): calcd. C 68.36, H 7.82, N 7.24; found C 68.33, H 7.71, N 6.87. − LRMS (EI): m/z = 193 [M$^+$], 178, 138.

3,4-Dimethyl-1-(1-methylpent-4-enyl)pyrrole-2,5-dione (12c): Dimethylmaleimide (0.914 g, 7.31 mmol) and 5-hexen-2-ol (0.8 g, 8.04 mmol) were reacted according to the general Mitsunobu procedure above to give the title product as an oil (0.76 g, 50%). − IR (film): $\tilde{\nu}$ = 2925, 1702, 1622 cm^{-1}. − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.82−5.68 (m, 1 H), 5.01−4.91 (m, 2 H), 3.45−3.25 (m, 1 H), 2.06−2.01 (m, 2 H), 1.94 (s, 6 H), 1.6−1.5 (m, 2 H), 1.35 (d, *J* = 7.0 Hz, 3 H). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 172.3 (C=O), 137.5 (C), 136.7 (CH), 114.9 (CH_2), 46.5 (CH), 32.8 (CH_2), 30.7 (CH_2), 18.4 (CH_3), 8.3 (CH_3). − $C_{12}H_{17}NO_2$ (207.27): calcd. C, 69.54, H 8.27, N 6.76; found C, 69.50, H 8.24, N 6.70. − LRMS (EI): *m*/*z* = 207 [M$^+$], 192, 179, 124, 83, 55.

3,4-Dimethyl-1-(2-methylpent-4-enyl)pyrrole-2,5-dione (12d): Dimethylmaleimide (1.05 g, 8.35 mmol) and 2-methyl-4-penten-1-ol[15] (0.92 g, 9.18 mmol) were reacted according to the general Mitsunobu procedure above to give the title product as an oil (1.25 g, 72%). − IR (film): $\tilde{\nu}$ = 2945, 1700, 1640 cm^{-1}. − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.83−5.69 (m, 1 H), 5.07−4.98 (m, 2 H), 3.39 (dd, *J* = 6.6, 13.8 Hz, 1 H), 3.29 (dd, *J* = 7.5, 13.8 Hz, 1 H), 2.12−1.83 (m, 3 H), 1.95 (s, 6 H), 0.85 (d, *J* = 6.5 Hz, 3 H). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 172.8 (C=O), 137.3 (C), 136.6 (CH), 116.5 (CH_2), 43.8 (CH_2), 38.9 (CH), 32.4 (CH_2), 17.3 (CH_3), 8.7 (CH_3). − LRMS (EI): *m*/*z* = 207 [M$^+$], 165, 138, 126, 111, 97, 83, 69, 57. − HRMS (EI): *m*/*z* = $C_{12}H_{17}NO_2$ calcd. 207.1259; found 207.1264.

3,4-Dimethyl-1-(3-methylpent-4-enyl)pyrrole-2,5-dione (12e): Dimethylmaleimide (0.152 g, 1.26 mmol) and 3-methyl-4-penten-1-ol[16] (0.139 mL, 1.38 mmol) were reacted according to the general Mitsunobu procedure above to give the title product as a clear oil (0.21 g, 81%). − IR (film): $\tilde{\nu}$ = 2935, 1772, 1704, 1639 cm^{-1}. − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.68−5.61 (m, 1 H), 4.97−4.85 (m, 2 H), 3.42 (t, *J* = 7.3 Hz, 2 H), 2.38−2.21 (m, 1 H), 1.64−1.54 (m, 2 H), 1.96 (s, 6 H), 0.97 (d, *J* = 7.2 Hz, 3 H). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 172.1 (C=O), 143.2 (CH), 136.9 (C), 113.4 (CH_2), 36.2 (CH_2), 35.5 (CH), 34.6 (CH_2), 20.1 (CH_3), 8.6 (CH_3). − $C_{12}H_{17}NO_2$ (207.27): calcd. C, 69.54, H 8.27, N 6.76; found C, 69.23, H 8.61, N 7.07. − LRMS (EI): *m*/*z* = 207 [M$^+$], 192, 178, 138, 126, 111, 97, 83, 69, 57.

3,4-Dimethyl-1-(4-methylpent-4-enyl)pyrrole-2,5-dione (12f): Dimethylmaleimide (1.14 g, 9.08 mmol) and 4-methyl-4-penten-1-ol[17] (1.0 g, 9.98 mmol) were reacted according to the general Mitsunobu procedure above to give the title product as an oil (1.48 g, 79%). − IR (film): $\tilde{\nu}$ = 2925, 1712, 1634 cm^{-1}. − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.80−4.73 (m, 2 H), 3.51 (t, 2 H, *J* = 7.2 Hz), 2.31−2.23 (m, 2 H), 1.96 (s, 6 H), 1.70−1.61 (m, 3 H), 1.50−1.39 (m, 2 H). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 172.7 (C=O), 138.9 (C), 136.3 (C), 110.5 (CH_2), 43.8 (CH_2), 34.2 (CH_2), 26.8 (CH_2), 22.5 (CH_3), 13.7 (CH_3). − $C_{12}H_{17}NO_2$ (207.27): calcd. C 69.54; H 8.27; N 6.76; found C 69.27, H 8.01, N 6.42. − LRMS (EI): *m*/*z* = 207 [M$^+$], 179, 152, 138, 126, 111, 97, 69, 57.

1-Hex-4-enyl-3,4-dimethylpyrrole-2,5-dione (12g): Dimethylmaleimide (0.65 g, 5.16 mmol) and *trans*-4-hexen-1-ol (0.67 mL, 5.67 mmol) were reacted according to the general Mitsunobu procedure above to give the title product as an oil (1.04 g, 97%). − IR (film): $\tilde{\nu}$ = 2935, 1700, 1628 cm^{-1}. − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.48−5.33 (m, 2 H), 3.47−3.45 (t, 2 H, *J* = 7.1 Hz), 1.98−1.94 (m + s, 2 H + 6 H), 1.67−1.57 (m, 5 H). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 172.2 (C=O), 136.9 (C), 129.8 (CH), 125.5 (CH), 37.2 (CH_2), 29.5 (CH_2), 28.0 (CH_2), 17.6 (CH_3), 8.3 (CH_3). − $C_{12}H_{17}NO_2$ (207.27): calcd. C 69.54, H 8.27, N 6.76; found C 69.48, H 8.24, N 6.74. − LRMS (EI): *m*/*z* = 207 [M$^+$],179, 166, 121, 111, 83, 68, 54.

3,4-Dichloro-1-pent-4-enylpyrrole-2,5-dione (32): Dichloromaleimide[18] (1 g, 6.03 mmol) and 4-penten-1-ol (0.57 g, 6.63 mmol) were reacted according to the general Mitsunobu procedure above to give the title product as a yellow oil (0.82 g, 59%). − IR (film): $\tilde{\nu}$ = 1795, 1725, 1643, 1622 cm^{-1}. − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.83−5.71 (m, 1 H), 5.09−4.99 (m, 2 H), 3.62 (t, 2 H, *J* = 7.3 Hz), 2.10−2.06 (m, 2 H), 1.78−1.69 (m, 2 H). − ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 167.9 (C=O), 141.6 (C), 138.1 (CH), 120.4 (CH_2), 35.3 (CH_2), 32.0 (CH_2), 25.6 (CH_2). − LRMS (EI): *m*/*z* = 233 [M$^+$], 203, 191, 178, 149, 111, 97, 83, 71, 57. − HRMS (EI): $C_9H_9Cl_2NO_2$ calcd. 233.0010; found 233.0003.

1-(2-Cyclopent-2-enylethyl)pyrrole-2,5-dione (19a): Maleimide (1.14 g, 11.8 mmol) and alcohol **17**[10] (1.36 g, 10.7 mmol) were reacted according to the general Mitsunobu procedure above to give the title product as an oil (1.4 g, 70%). − IR (neat): $\tilde{\nu}$ = 1769, 1710 cm^{-1}. − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.68 (s, 2 H), 5.77−5.72 (m, 1 H), 5.69−5.64 (m, 1 H), 3.56 (t, 2 H, *J* = 7.4 Hz), 2.66−2.58 (m, 1 H), 2.37−2.24 (m, 2 H), 2.15−2.02 (m, 1 H), 1.78−1.39 (m, 3 H). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.7 (C=O), 134.0 (CH), 133.8 (CH), 131.0 (CH), 42.9 (CH), 36.5 (CH_2), 34.3 (CH_2), 31.9 (CH_2), 29.4 (CH_2). − $C_{11}H_{13}NO_2$ (191.23): calcd. C 69.11, H 6.81, N 7.32; found C 69.12, H 6.81, N 7.56. − LRMS (EI): *m*/*z* = 191 [M$^+$], 110, 99, 93, 67.

1-(2-Cyclopent-2-enylethyl)-3,4-dimethylpyrrole-2,5-dione (19b): Dimethylmaleimide (0.190 g, 1.52 mmol) and alcohol **17** (0.170 g, 1.52 mmol) were reacted according to the general Mitsunobu procedure above to give the title product as an oil (0.219 g, 66%). − IR (neat): $\tilde{\nu}$ = 2940, 2850, 1770, 1700 cm^{-1}. − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.75−5.65 (m, 2 H), 3.52 (t, *J* = 7.4 Hz, 2 H), 2.66−2.54 (m, 1 H), 2.41−2.21 (m, 2 H), 2.12−2.02 (m, 1 H), 1.96 (s, 6 H), 1.76−1.35 (m, 3 H). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 172.3 (C=O), 137.0 (CH), 134.0 (CH), 130.9 (C), 42.8 (CH), 36.4 (CH_2), 34.4 (CH_2), 31.8 (CH_2), 29.3 (CH_2), 8.4 (CH_3). − $C_{13}H_{17}NO_2$ (219.28): calcd. C 71.19, H 7.82, N 6.39; found C 71.06, H 7.85, N 6.26. − LRMS (EI): *m*/*z* = 219 [M$^+$], 139, 127.

2-(2-Cyclopent-2-enylethyl)-4,5,6,7-tetrahydroisoindole-1,3-dione (19c): THPI (1.6 g, 10.7 mmol) and alcohol **17** (1 g, 9 mmol) were reacted according to the general Mitsunobu procedure above to give the title product as an oil (1.42 g, 64%). − IR (neat): $\tilde{\nu}$ = 3050, 2935, 1765, 1700, 1615 cm^{-1}. − ^{1}H NMR (300 MHz, $CDCl_3$) δ = 5.76−5.66 (m, 2 H), 3.51 (t, *J* = 7.3 Hz, 2 H), 2.67−2.56 (m, 1 H), 2.82−2.35 (m, 6 H), 2.25−2.20 (m, 1 H), 1.85−1.40 (m, 7 H). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 171.3 (C=O), 141.5 (C), 134.1 (CH), 130.9 (CH), 42.9 (CH), 42.8 (CH_2), 36.1 (CH_2), 34.6 (CH_2), 31.7 (CH_2), 29.4 (CH_2), 21.2 (CH_2). − $C_{15}H_{19}NO_2$ (245.32): calcd. C 73.43, H 7.81, N 5.71; found C 73.33, H 7.78, N 5.70. − LRMS (EI): *m*/*z* = 245 [M$^+$], 164, 153.

1-(2-Cyclohex-2-enylethyl)-3,4-dimethylpyrrole-2,5-dione (19d): Dimethylmaleimide (0.193 g, 1.54 mmol) and alcohol **18**[11] (0.194 g, 1.54 mmol) were reacted according to the general Mitsunobu procedure above to give the title product as an oil (0.246 g, 68%). − IR (neat): $\tilde{\nu}$ = 2930, 2860, 1770, 1700, 1650 cm^{-1}. − ^{1}H NMR (270 MHz, $CDCl_3$): δ = 5.70−5.55 (m, 2 H), 3.54 (t, *J* = 7.4 Hz, 2 H), 1.95 (s, 6 H), 2.19−1.20 (m, 9 H). − ^{13}C NMR (67.5 MHz, $CDCl_3$): δ = 172.2 (C=O), 137.0 (C), 130.7 (CH), 127.6 (CH), 35.7 (CH_2), 34.8 (CH_2), 32.6 (CH), 28.6 (CH_2), 25.2 (CH_2), 21.2 (CH_2), 8.6 (CH_3). − LRMS (EI): *m*/*z* = 233 [M$^+$], 267, 138.

1-(2-Allylcyclopentyl)-3,4-dimethylpyrrole-2,5-dione (23): Dimethylmaleimide (0.9 g, 7.2 mmol) and alcohol **21**[12] (1.0 g, 7.9 mmol) were reacted according to the general Mitsunobu procedure above to give the title product as an oil (1.2 g, 65%). − IR (film): $\tilde{\nu}$ =

2952, 1700, 1640 cm^{-1}. − ^{1}H NMR (270 MHz, CDCl$_3$): δ = 1.2−2.2 (m, 15 H), 4.5 (unresol. dd, 1 H), 4.8−4.9 (m, 2 H), 5.5−5.8 (m, 1 H). − ^{13}C (67.5 MHz, CDCl$_3$): δ = 8.4 (CH$_3$), 24.0 (CH$_2$), 28.4 (CH$_2$), 31.5 (CH$_2$), 34.6 (CH$_2$), 43.1 (CH), 52.7 (CH), 114.8 (CH$_2$), 136.5 (C), 137.6 (CH), 172.8 (C=O). − LRMS (EI): *m/z* = 233 [M$^+$], 164, 152, 126, 108, 93. − HRMS (EI): calcd. for $C_{14}H_{19}NO_2$ 233.1416; found 233.1412.

1-(2-Allylcyclohexyl)-3,4-dimethylpyrrole-2,5-dione (26): Dimethylmaleimide (0.81 g, 6.5 mmol) and alcohol **22**[13] (1.0 g, 7.1 mmol) were reacted according to the general Mitsunobu procedure above to give the title product as a white solid (1.1 g, 62%); M.p. 56 −57 °C. − IR (film): ṽ = 2952, 1700, 1632 cm^{-1}. − ^{1}H NMR (270 MHz, CDCl$_3$): δ = 1.2−2.4 (m, 17 H), 4.1 (dt, *J* = 13, 4 Hz, 1 H), 4.82−4.96 (m, 2 H), 5.46−5.62 (m, 1 H). − ^{13}C (67.5 MHz, CDCl$_3$): δ = 8.65 (CH$_3$), 19.8 (CH$_2$), 24.8 (CH$_2$), 26.3 (CH$_2$), 27.9 (CH$_2$), 31.3 (CH$_2$), 38.3 (CH), 54.8 (CH), 115.6 (CH$_2$), 136.6 (C=C), 137.5 (CH), 172.9 (C=O). − $C_{15}H_{21}NO_2$ (247.34): calcd. C 72.87, H 8.50, N 5.67; found C 73.12, H 8.55, N 5.44. − LRMS (EI): *m/z* = 247 [M$^+$], 165, 164, 138.

3,4-Dimethyl-1-[2-(2-methylenecyclohexyl)ethyl]pyrrole-2,5-dione (29): Dimethylmaleimide (1.3 g, 10 mmol) and alcohol **28**[14] (1.5 g, 11 mmol) were reacted according to the general Mitsunobu procedure above to give the title product as an oil (1.7 g, 68%). − IR (film): ṽ = 2929, 2854, 1700, 1645 cm^{-1}. − ^{1}H NMR (270 MHz, CDCl$_3$): δ = 1.2−2.2 (17 H, m), 3.44−3.54 (m, 2 H), 4.60 (s, 1 H), 4.71 (s, 1 H). − ^{13}C (67.5 MHz, CDCl$_3$): δ = 8.3 (CH$_3$), 23.9 (CH$_2$), 28.8 (CH$_2$), 30.7 (CH$_2$), 33.7 (CH$_2$), 34.4 (CH$_2$), 36.1 (CH$_2$), 40.6 (CH), 106.0 (CH$_2$), 136.8 (C), 136.9 (C), 172.2 (C=O). − LRMS (EI): *m/z* = 247 (27) [M$^+$], 221 (47), 138 (82), 126 (39), 122 (100). − HRMS (EI): $C_{15}H_{21}NO_2$ calcd. 247.1572; found 247.1564.

General Photolysis Procedure: A solution of the alkenylimide in acetonitrile (100 mL) was placed in a 150 mL pyrex immersion-well photoreactor and degassed for 10 min. by bubbling nitrogen through the solution with a long syringe needle. The solution was irradiated under an atmosphere of nitrogen for the appropriate period of time using a 125 W medium pressure Hg-lamp. After the reaction was complete (TLC control) the solvent was removed under reduced pressure and the resultant crude photocycloadduct purified by flash column chromatography over silica gel using the solvent system stated.

2,3,6,7,8,9,11,11a-Octahydro-1*H*-benzo[*e*]pyrrolo[1,2-*a*]azepine-5,10-dione (11): of 2-Pent-4-enyl-4,5,6,7-tetrahydroisoindole-1,3-dione (**9**; 0.5 g, 2.28 mmol) was subjected to the general photolysis procedure (90 min.). Purification by flash chromatography (50% EtOAc/petroleum ether) gave the title compound as a white solid (0.46 g, 92%). − M.p. 82−85 °C. − IR (nujol): ṽ = 1683, 1643, 1601 cm^{-1}. − ^{1}H NMR (300 MHz, CDCl$_3$): δ = 4.32−4.21 (m, 1 H), 3.72−3.53 (m, 2 H), 2.96−2.64 (m, 4 H), 2.30−1.91 (m, 5 H), 1.80−1.59 (m, 5 H). − ^{13}C NMR (75 MHz, CDCl$_3$): δ = 202.1 (C=O), 166.5 (C=O), 141.4 (C), 139.6 (C), 52.3 (CH), 51.9 (CH$_2$), 46.1 (CH$_2$), 31.3 (CH$_2$), 27.5 (CH$_2$), 25.7 (CH$_2$), 23.1 (CH$_2$), 21.6 (CH$_2$), 21.5 (CH$_2$). − $C_{13}H_{17}NO_2$ (219.28): calcd. C 71.19, H 7.82, N 6.39; found C 71.13, H 7.85, N 6.11. − LRMS (EI): *m/z* = 219 [M$^+$], 191.1, 163, 108.

2,3,9,9a-Tetrahydro-1*H*-pyrrolo[1,2-*a*]azepine-5,8-dione (13a): Maleimide **12a** (0.165 g, 1 mmol) was subjected to the general photolysis procedure (20 min.) to give the title compound as an oil (0.085 g, 51%) after purification by flash chromatography (70−90% EtOAc/petroleum ether). − IR (neat): ṽ = 3200, 1700, 1685, 1641, 1601 cm^{-1}. − ^{1}H NMR (300 MHz, CDCl$_3$): δ = 6.58 (d, *J* = 12.9 Hz, 1 H), 6.29 (d, *J* = 12.9 Hz, 1 H), 4.22−4.15 (m, 1 H), 3.80 (dt, *J* = 12.5, 6.0 Hz, 1 H), 3.61 (dt, *J* = 12.5, 6.9 Hz, 1 H), 2.90−2.70 (m, 2 H), 2.39−2.26 (m, 1 H), 2.07−1.70 (m, 3 H). − ^{13}C NMR (75 MHz, CDCl$_3$): δ = 198.3 (C=O), 163.1 (C=O), 136.6 (CH), 134.0 (CH), 53.3 (CH), 49.8 (CH$_2$), 47.1 (CH$_2$), 33.1 (CH$_2$), 23.3 (CH$_2$). − $C_9H_{11}NO_2$ (165.19): calcd. C 65.42, H 6.72, N 8.47; found C 65.18, H 6.69, N 8.18. − LRMS (EI): *m/z* = 165 [M$^+$], 84.

6,7-Dimethyl-2,3,9,9a-tetrahydro-1*H*-pyrrolo[1,2-*a*]azepine-5,8-dione (13b): Maleimide **12b** (0.201 g, 1.05 mmol) was subjected to the general photolysis procedure (2.5 h) to give the title product as a white solid (0.199 g, 99%) after purification by flash chromatography (90% EtOAc/petroleum ether). − M.p. 81 °C. − IR (neat): ṽ = 3580, 2955, 1670, 1635, 1605 cm^{-1}. − ^{1}H NMR (300 MHz, CDCl$_3$): δ = 4.29−4.18 (m, 1 H), 3.69−3.46 (m, 2 H), 2.72 (dd, *J* = 18.8, 11.4 Hz, 1 H), 2.64 (dd, *J* = 18.8, 3.7 Hz, 1 H), 2.24−2.10 (m, 1 H), 2.02 (s, 3 H), 1.96−1.84 (m, 2 H), 1.89 (s, 3 H), 1.75−1.66 (m, 1 H). − ^{13}C NMR (75 MHz, CDCl$_3$): δ = 202.5 (C=O), 166.8 (C=O), 139.3 (C), 138.3 (C), 52.3 (CH), 51.7 (CH$_2$), 45.9 (CH$_2$), 30.9 (CH$_2$), 22.9 (CH$_2$), 17.6 (CH$_3$), 15.9 (CH$_3$). − $C_{11}H_{15}NO_2$ (193.24): calcd. C 68.35, H 7.83, N 7.25; found C 68.23, H 7.65, N 6.95. − LRMS (EI): *m/z* = 193 [M$^+$] 178, 138, 124.

3,6,7-Trimethyl-2,3,9,9a-tetrahydro-1*H*-pyrrolo[1,2-*a*]azepine-5,8-dione (13c): The maleimide **12c** (0.43 g, 2.06 mmol) was subjected to the general photolysis procedure (2.5 h) to give the title product as an inseparable 1.27:1 mixture of diastereoisomers (0.296 g, 69%) after purification by flash column chromatography (50% EtOAc/petroleum ether). − IR (film): ṽ = 2956, 1674, 1627, 1618 cm^{-1}. − ^{1}H NMR (300 MHz, CDCl$_3$): δ = 4.36−4.11 (m, 1 H), 4.06−3.92 (m, 2 H), 3.10−2.62 (m, 3 H), 2.49−2.14 (m, 2 H), 1.98 (s, 3 H), 1.95 (s, 3 H), 1.14 (major) and 1.12 (minor) (2 × d, *J* = 6.5 and 6.6 Hz, 3 H). − ^{13}C NMR (75 MHz, CDCl$_3$): δ = 202.6 (C=O), 202.4 (C=O), 166.7 (C=O), 166.3 (C=O), 140.6 (C), 139.2 (C), 138.6 (C), 137.1 (C), 54.5 (CH), 53.8 (CH$_2$), 53.6 (CH), 53.2 (CH), 53.1 (CH), 51.8 (CH$_2$), 31.4 (CH$_2$), 29.8 (CH$_2$), 29.7 (CH$_2$), 28.7 (CH$_2$), 20.6 (CH$_3$), 19.1 (CH$_3$), 18.3 (CH$_3$), 17.9 (CH$_3$), 16.4 (CH$_3$), 15.7 (CH$_3$). − $C_{12}H_{17}NO_2$ (207.27): calcd. C 69.54, H 8.27, N 6.76; found C 69.26, H 8.12, N 6.54. − LRMS (EI): *m/z* = 207 [M$^+$], 179, 164, 138, 124, 110, 84, 54.

2,6,7-Trimethyl-2,3,9,9a-tetrahydro-1*H*-pyrrolo[1,2-*a*]azepine-5,8-dione (13d): The maleimide **12d** (0.5 g, 2.41 mmol) was subjected to the general photolysis procedure (6 h) after which purification by flash column chromatography (50% EtOAc/petroleum ether) gave the title product as an inseparable 1:1 mixture of diastereoisomers (0.43 g, 87%). − IR (film): ṽ = 2965, 1670, 1620 cm^{-1}. − ^{1}H NMR (300 MHz, CDCl$_3$): δ = 4.39−4.10 (m, 1 H), 4.03−3.87 (m, 2 H), 3.18−2.75 (m, 3 H), 2.49−2.14 (m, 2 H), 2.10−2.04 (br.s, 3 H), 1.87−1.83 (br.s, 3 H), 1.12 and 1.10 (2 × d, *J* = 3.6 and 3.6 Hz, 3 H). − ^{13}C NMR (75.5 MHz, CDCl$_3$): δ = 202.9 (C=O), 201.7 (C=O), 167.1 (C=O), 166.9 (C=O), 140.3 (C), 139.3 (C), 138.6 (C), 138.2 (C), 52.99 (CH$_2$), 52.95 (CH$_2$), 52.70 (CH), 52.61 (CH$_2$), 52.26 (CH$_2$), 40.83 (CH$_2$), 39.02 (CH$_2$), 32.48 (CH), 30.78 (CH), 18.65 (CH$_3$), 17.80 (CH$_3$), 17.59 (CH$_3$), 17.10 (CH$_3$), 16.22 (CH$_3$), 16.03 (CH$_3$). − LRMS (EI): 207 [M$^+$], 164, 138, 124, 110, 96, 84, 68, 54. − HRMS (EI): $C_{12}H_{17}NO_2$ calcd. 207.1259; found 207.1257.

1,6,7-Trimethyl-2,3,9,9a-tetrahydro-1*H*-pyrrolo[1,2-*a*]azepine-5,8-dione (13e): The maleimide **12e** (0.5 g, 2.41 mmol) was subjected to the general photolysis procedure (4 h) after which purification by flash column chromatography (50% EtOAc/petroleum ether) gave the title product as an inseparable 3:1 mixture of diastereoisomers (0.45 g, 90%). − IR (film): ṽ = 2965, 1678, 1616, 1519, 1455, 1094 cm^{-1}. − ^{1}H NMR (300 MHz, CDCl$_3$): δ = 4.18−4.1 (m, 1 H, minor isomer), 3.76−3.62 (m, 2 H), 3.52−3.43 (m, 1 H, major), 3.37−3.29 (m, 1 H, minor), 2.77−2.48 (2 overlapping ABX systems, J_{major} = 11, 7 Hz, 2 H), 2.47−2.6 (m, 1 H, minor), 2.06−1.97 (4 H, br.s + m), 1.88 (3 H, br.s), 2.16−1.87 (m, 1 H), 1.62−1.45 (m, 2 H), 1.12 (major) + 1.03 (minor) (2 × d, J = 6.2 and 6.2 Hz, 3 H). − ^{13}C NMR (75 MHz, CDCl$_3$): δ = 202.5 (C=O), 201.8 (C=O), 166.7 (C=O), 139.9 (C), 139.3 (C), 138.6 (C), 138.1 (C), 59.4 (CH), 55.8 (CH), 51.2 (CH$_2$), 46.8 (CH$_2$), 45.2 (CH$_2$), 45.1 (CH$_2$), 39.8 (CH), 35.8 (CH), 31.2 (CH$_2$), 30.3 (CH$_2$), 18.4 (CH$_3$), 18.2 (CH$_3$), 17.4 (CH$_3$), 16.2 (CH$_3$), 16.1 (CH$_3$), 14.10 (CH$_3$). − C$_{12}$H$_{17}$NO$_2$ (207.27): HRMS (EI): *m/z* C$_{12}$H$_{17}$NO$_2$ calcd. 207.1259; found 207.1263. − LRMS (EI): *m/z* = 207 [M$^+$], 192, 179, 164, 152, 138, 124, 101, 96, 83, 70, 55.

6,7,9a-Trimethyl-2,3,9,9a-tetrahydro-1*H*-pyrrolo[1,2-*a*]azepine-5,8-dione (13f): The maleimide **12f** (0.5 g, 2.41 mmol) was subjected to the general photolysis procedure (24 h), which after purification by flash column chromatography (50% EtOAc/petroleum ether) gave the title compound as an oil (0.18 g, 33%). − IR (film): ṽ = 2955, 1680, 1630, 1604 cm^{-1}. − ^{1}H NMR (300 MHz, CDCl$_3$): δ = 3.79 (m, 2 H), 3.23 (d, J = 18 Hz, 1 H), 3.01 (d, J = 18 Hz, 1 H), 2.11−1.95 (m, 4 H), 1.96 (s, 3 H), 1.93 (s, 3 H), 1.21 (s, 3 H). − ^{13}C NMR (75.5 MHz, CDCl$_3$): δ = 203 (C=O), 167.4 (C=O), 137.2 (C), 130.5 (C), 55.2 (C), 52.5 (CH$_2$), 50.2 (CH$_2$), 31.5 (CH$_2$), 23.8 (CH$_2$), 19.6 (CH$_3$), 15.8 (CH$_3$), 15.4 (CH$_3$). − C$_{12}$H$_{17}$NO$_2$ (207.27): calcd. C 69.54, H 8.27, N 6.76; found C 69.24, H 7.99, N 6.21. − LRMS (EI): *m/z* = 207 [M$^+$], 179, 164, 138, 124, 110, 84, 54.

6,7,9-Trimethyl-2,3,9,9a-tetrahydro-1*H*-pyrrolo[1,2-*a*]azepine-5,8-dione (13g): The maleimide **12g** (0.3 g, 1.47 mmol) was subjected to the general photolysis procedure (4 h), which after purification by flash column chromatography (50% EtOAc/petroleum ether) gave the title compound as an oil (0.27 g, 88%). − IR (film): ṽ = 2976, 2878, 1685, 1637, 1608 cm^{-1}. − ^{1}H NMR (270 MHz, CDCl$_3$): δ = 3.92−3.84 (m, 1 H), 3.66−3.45 (m, 2 H), 2.72−2.56 (m, 2 H), 2.21−1.79 (m, 3 H), 1.98 (s, 3 H), 1.96 (s, 3 H), 1.09 (d, J = 7.1 Hz, 3 H). − ^{13}C NMR (75.5 MHz, CDCl$_3$): δ = 208.3 (C=O), 167.4 (C=O), 138.3 (C), 136.1 (C), 58.3 (CH), 56.6 (CH), 45.7 (CH$_2$), 29.0 (CH$_2$), 22.7 (CH$_2$), 17.0 (CH$_3$), 15.9 (CH$_3$), 15.7 (CH$_3$). − C$_{12}$H$_{17}$NO$_2$ (207.27): calcd. C 69.54, H 8.27, N 6.76; found C 69.36, H 8.20, N 6.67. − LRMS (EI): *m/z* = 207 [M$^+$], 179, 164, 138, 125, 85, 55.

6,7-Dichloro-2,3,9,9a-tetrahydro-1*H*-pyrrolo[1,2-*a*]azepine-5,8-dione (33): The maleimide **32** (0.5 g, 2.14 mmol) was subjected to the general photolysis procedure (2.5 h), which after purification by flash column chromatography (50% EtOAc/petroleum ether) gave the title compound as a white solid (0.33 g, 66%). − M.p. 149−150 °C. − IR (film): ṽ = 1694, 1649 cm^{-1}. − ^{1}H NMR (300 MHz, CDCl$_3$): δ = 4.44−4.35 (m, 1 H), 3.74−3.69 (m, 2 H), 3.01−2.87 (m, 2 H), 2.40−2.28 (m, 1 H), 2.07−1.97 (m, 2 H), 1.87−1.78 (m, 1 H). − ^{13}C NMR (75 MHz, CDCl$_3$): δ = 190.8 (C=O), 158.2 (C=O), 139.2 (C), 136.8 (C), 52.5 (CH), 50.5 (CH$_2$), 47.4 (CH$_2$), 31.4 (CH$_2$), 23.0 (CH$_2$). − LRMS (EI): *m/z* = 233, 198, 170, 142, 87, 70, 57. − HRMS (EI): *m/z* C$_9$H$_9$NCl$_2$O$_2$ calcd. 233.0010; found 233.0006.

2,2a,3,4,8a,8b-Hexahydro-1*H*-4a-azacyclopenta[*cd*]azulene-5,8-dione (20a): The maleimide **19a** (0.5 g, 2.62 mmol) was subjected to the general photolysis procedure (20 min.), which after purification by flash column chromatography (50% EtOAc/petroleum ether) gave the title compound as a white solid (0.25 g, 50%). − M.p. 134 °C. − IR (nujol): ṽ = 1675, 1635, 1610 cm^{-1}. − ^{1}H NMR (270 MHz, CDCl$_3$): δ = 6.61 (d, J = 13 Hz, 1 H), 6.25 (d, J = 13 Hz, 1 H), 4.50 (t, J = 5.6 Hz, 1 H), 3.89−3.83 (m, 1 H), 3.57−3.42 (m, 1 H), 3.08−2.91 (m, 2 H), 2.35−1.53 (m, 6 H). − ^{13}C NMR (75 MHz, CDCl$_3$): δ = 198.6 (C=O), 167.8 (C=O), 141.1 (CH), 137.1 (CH), 64.1 (CH), 62.6 (CH), 57.8 (CH$_2$), 48.2 (CH), 31.9 (CH$_2$), 30.3 (CH$_2$), 27.8 (CH$_2$). − C$_{11}$H$_{17}$NO$_2$ (191.23): calcd. C 69.11, H 6.81, N 7.32; found C 69.39, H 6.70, N 6.71. − LRMS (EI): *m/z* = 191 [M$^+$], 163, 136, 86.

6,7-Dimethyl-2,2a,3,4,8a,8b-hexahydro-1*H*-4a-azacyclopenta[*cd*]azulene-5,8-dione (20b): The maleimide **19b** (0.122 g, 0.56 mmol) was subjected to the general photolysis procedure (2 h), which after purification by flash column chromatography (90% EtOAc/petroleum ether) gave the title product as a white solid (0.101 g, 83%). − M.p. 122 °C. − IR (nujol): ṽ = 1675, 1635, 1610 cm^{-1}. − ^{1}H NMR (270 MHz, CDCl$_3$): δ = 4.43 (t, 1 H, J = 6.6 Hz), 3.80−3.65 (m, 1 H), 3.50−3.40 (m, 1 H), 3.10−2.92 (m, 2 H), 2.19−1.59 (m, 6 H), 1.97 (s, 3 H), 1.94 (s, 3 H). − ^{13}C NMR (75 MHz, CDCl$_3$): δ = 204.9 (C=O), 167.8 (C=O), 141.1 (C), 134.6 (C), 62.7 (CH), 61.8 (CH), 46.3 (CH$_2$), 43.2 (CH), 31.0 (CH$_2$), 30.0 (CH$_2$), 24.5 (CH$_2$), 16.2 (CH$_3$), 15.8 (CH$_3$). − C$_{13}$H$_{17}$NO$_2$ (219.28): calcd. C 71.19, H 7.82, N 6.39; found C 70.83, H 7.89, N 6.29. − LRMS (EI): *m/z* = 219 [M$^+$], 204, 139, 127.

2,2a,3,4,6,7,8,9,10a,10b-Decahydro-1*H*-4a-azabenzo[*g*]cyclopenta[*cd*]azulene-5,10-dione (20c): The maleimide **19c** (0.220 g, 0.9 mmol) was subjected to the general photolysis procedure (2.5 h), which after purification by flash column chromatography (70% EtOAc/petroleum ether) gave the title product as a white solid (0.195 g, 89%). − M.p. 150 °C. − IR (nujol): ṽ = 1690, 1640, 1610 cm^{-1}. − ^{1}H NMR (300 MHz, CDCl$_3$): δ = 4.45 (dd, J = 6.5, 6.4 Hz, 1 H), 3.88−3.64 (m, 1 H), 3.50−3.38 (m, 1 H), 3.12−2.52 (m, 4 H), 2.20−1.65 (m, 12 H). − ^{13}C NMR (75 MHz, CDCl$_3$): δ = 204.5 (C), 167.5 (C), 142.9 (C), 136.4 (C), 62.5 (CH), 61.8 (CH), 46.2 (CH$_2$), 43.1 (CH), 30.9 (CH$_2$), 29.9 (CH$_2$), 25.9 (CH$_2$), 25.5 (CH$_2$), 24.5 (CH$_2$), 21.3 (CH$_2$), 21.2 (CH$_2$). − C$_{15}$H$_{19}$NO$_2$ (245.32): calcd. C 73.43, H 7.81, N 5.71; found C 73.13, H 7.80, N 5.59. − LRMS (EI): *m/z* = 245 [M$^+$], 217, 153.

5,6-Dimethyl-1,2,7a,8,9,10,10a,10b-octahydroazepino[3,2,1-*hi*]indole-4,7-dione (20d): The maleimide **19d** (0.140 g, 0.6 mmol) was subjected to the general photolysis procedure (2.5 h), which after purification by flash column chromatography (70% EtOAc/petroleum ether) gave the title product as an oil (0.127 g, 90%). − IR (neat): ṽ = 3435, 2931, 1684, 1640, 1617cm^{-1}. − ^{1}H NMR (270 MHz, CDCl$_3$): δ = 4.31 (t, J = 5.5 Hz, 1 H), 4.05 (ddd, J = 11.9, 7.8, 1.4 Hz, 1 H), 3.50−3.38 (m, 1 H), 2.60−2.40 (m, 2 H), 2.20−2.10 (m, 1 H), 1.99 (s, 3 H), 1.97 (s, 3 H), 1.90−1.57 (m, 4 H), 1.31−1.12 (m, 3 H). − ^{13}C NMR (75 MHz, CDCl$_3$): δ = 205.3 (C=O), 169.9 (C=O), 139.3 (C), 135.1 (C), 54.9 (CH), 54.7 (CH), 46.2 (CH$_2$), 37.4 (CH), 30.4 (CH$_2$), 27.1 (CH$_2$), 22.2 (CH$_2$), 21.1 (CH$_2$), 16.7 (CH$_3$), 16.6 (CH$_3$). − LRMS (EI): *m/z* = 233 [M$^+$], 207, 179, 138. − HRMS (EI): C$_{14}$H$_{19}$NO$_2$ calcd. 233.1416 found 233.1422.

***cis*- and *trans*-5,6-Dimethyl-1,2,3,3a,8,8a,9,9a-octahydro-3b-azacyclopenta[*a*]azulene-4,7-dione (24, 25):** The maleimide **23** (0.3 g, 1.3 mmol) was subjected to the general photolysis procedure (1 h) to give the *trans* product **25** as a yellow oil (0.059 g, 20%) after flash chromatography (70% ethyl acetate/petroleum ether). − IR (neat): ṽ = 2950, 2867, 1700, 1634 cm^{-1}. − ^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.2−2.2 (m, 15 H), 2.7 (dd, J = 19, 12.5 Hz, 1 H), 2.72−2.83 (m, 1 H), 4.25−4.40 (m, 2 H). − ^{13}C (75 MHz, CDCl$_3$): δ = 15.3 (CH$_3$), 17.9 (CH$_3$), 23.7 (CH$_2$), 30.7 (CH$_2$), 32.4 (CH$_2$), 35.9 (CH_2), 40.4 (CH), 51.4 (CH_2), 54.9 (CH), 62.8 (CH), 137.1 (C), 140.8 (C), 166.8 (C=O), 202.4 (C=O). − LRMS: *m/z* = 233 [M^+], 205, 190, 176, 124, 110, 67. − HRMS (EI): $C_{14}H_{19}NO_2$ M^+ calcd. 233.1416; found 233.1416.

Further elution gave the *cis* product **24** as a clear oil (0.19 g, 63%). − IR (neat): $\tilde{\nu}$ = 2952, 1674, 1635 cm^{-1}. − ^1H NMR (500 MHz, $CDCl_3$): δ = 1.45 (dt, *J* = 6.8, 2.5 Hz, 1 H), 1.55−1.70 (m, 3 H), 1.74−1.81 (m, 1 H), 1.88 (q, *J* = 0.5 Hz, 3 H), 1.96−2.04 (m, 4 H), 2.43 (dt, *J* = 6.8, 4.6 Hz, 1 H), 2.66−2.70 (m, 2 H), 2.69 (dd, *J* = 9.3, 1.6 Hz, 1 H), 2.8 (dd, *J* = 9.3, 6.1 Hz, 1 H), 4.28 (dddd, *J* = 1.6, 2.5, 4.5, 6.2 Hz, 1 H), 4.38 (dt, *J* = 3.9, 1.7 Hz, 1 H). − ^{13}C (75 MHz, $CDCl_3$): δ = 16.1 (CH_3), 17.4 (CH_3), 24.6 (CH_2), 32.5 (CH_2), 33.7 (CH_2), 36.5 (CH_2), 41.4 (CH), 53.5 (CH_2), 53.9 (CH), 64.6 (CH), 138.4 (C), 138.8 (C), 166.5 (C=O), 202.6 (C=O). − LRMS: *m/z* = 233 [M^+], 204, 190, 124, 67, 39. − HRMS: $C_{14}H_{19}NO_2$ M^+ calcd. 233.1416; found 233.1421.

***cis*- and *trans*-7,8-Dimethyl-2,3,4,4a,10,10a,11,11a-octahydro-1*H*-azepino[1,2-*a*]indole-6,9-dione (27):** The maleimide **26** (0.1 g, 0.4 mmol) was subjected to the general photolysis procedure (2 h) to give the title products as an inseparable 1:1 mixture of diastereomers, as a yellow oil (0.09 g, 90%) after flash chromatography (70% ethyl acetate/petroleum ether). − IR (neat): $\tilde{\nu}$ = 2929, 1771, 1629, 1607 cm^{-1}. − ^1H NMR (300 MHz, $CDCl_3$): δ = 1.0−3.0 (m, 18 H), 2.38 (dd, *J* = 19, 3 Hz, 0.5 H), 2.7 (dd, *J* = 18, 2 Hz, 0.5 H), 2.83 (dd, *J* = 19, 8 Hz, 0.5 H), 2.85 (dd, *J* = 19, 5 Hz, 0.5 H), 4.05−4.28 (m, 2 H). − ^{13}C (75 MHz, $CDCl_3$): δ = 15.7 (CH_3), 16.1 (CH_3), 18.1 (CH_3), 18.2 (CH_3), 20.3 (CH_2), 20.7 (CH_2), 23.3 (CH_2), 23.9 (CH_2), 25.5 (CH_2), 25.6 (CH_2), 26.6 (CH_2), 28.8 (CH_2), 32.3 (CH_2), 33.5 (CH_2), 34.1 (CH), 35.9 (CH), 51.8 (CH), 51.9 (CH), 52.5 (CH_2), 53.8 (CH_2), 57.0 (CH), 57.4 (CH), 137.1 (C), 137.9 (C), 139.2 (C), 139.8 (C), 166.2 (C=O), 166.3 (C=O), 201.9 (C=O), 202.5 (C=O). − LRMS: *m/z* = 247 [M^+], 219, 176, 124, 81, 67. − HRMS: $C_{15}H_{22}NO_2$ M^+ calcd. 247.1572; found 247.1571.

Azepine 30 and Cyclobutane 31: The maleimide **29** (1 g, 4.0 mmol) was subjected to the general photolysis procedure (7 h), which after purification by column chromatography (70% ethyl acetate/petroleum ether) gave **31** as a white solid (0.75 g, 75%). − M.p. 153−154 °C. − IR (liquid film): $\tilde{\nu}$ = 2997, 2934, 1708, 1452 cm^{-1}. − ^1H NMR (300 MHz, $CDCl_3$): δ = 1.2−1.8 (m, 17 H), 1.9 (d, *J* = 13 Hz, 1 H), 2.1 (d, *J* = 13 Hz, 1 H), 3.7 (m, 2 H). − ^{13}C (75 MHz, $CDCl_3$): δ = 8.4 (CH_3), 15.2 (CH_3), 22.6 (CH_2), 25.7 (CH_2), 33.3 (CH_2), 34.4 (CH_2), 35.4 (CH_2), 38.4 (CH_2), 41.2 (CH), 44.1 (C), 44.4 (CH_2), 44.8 (C), 56.8 (C), 184.0 (C=O), 189.4 (C=O). − LRMS: *m/z* = 247 [M^+], 139, 122, 93, 67. − HRMS (EI): $C_{15}H_{21}NO_2$ M^+ calcd. 247.1572; found 247.1565. − $C_{15}H_{21}NO_2$ (247.16): calcd. C 73.56, H 8.81, N 5.36; found C 73.85, H 9.28, N 5.37%.

Further elution with 70% ethyl acetate/petroleum ether gave **30** as an oil which solidified on standing (0.2 g, 20%). − M.p. 53−56 °C. − IR (CH_2Cl_2): $\tilde{\nu}$ = 2937, 2863, 1694, 1655 cm^{-1}. − ^1H NMR (300 MHz, $CDCl_3$): δ = 1.0−2.2 (m, 17 H), 2.76 (dd, *J* = 17, 1 Hz, 1 H), 3.2 (d, *J* = 17 Hz, 1 H), 3.55−3.75 (m, 2 H). − ^{13}C (75 MHz, $CDCl_3$): δ = 15.3 (CH_3), 20.3 (CH_3), 20.7 (CH_2), 22.2 (CH_2), 24.7 (CH_2), 25.7 (CH_2), 29.3 (CH_2), 46.2 (CH), 47.1 (CH_2), 52.1 (CH_2), 58.6 (C), 136.4 (C=C), 142.9 (C=C), 165.7 (C=O), 197.8 (C=O). − LRMS: *m/z* = 247 [M^+], 233, 219, 204, 176, 136, 124, 123, 122, 95. − HRMS: $C_{13}H_{21}NO_2$ M^+ calcd. 247.1572; found 247.1569.

Hexahydropyrrolo[1,2-*a*]azepine-5,8-dione (34): Zinc dust (3.2 g, 50 mmol) was added to glacial acetic acid (15 mL) and the resulting suspension stirred for 20 min. at room temperature. Dichloroazepine **33** (0.5 g, 2.47 mmol) in glacial acetic acid (5 mL) was added to this suspension dropwise over 20 min. and the reaction mixture stirred for a further 1.5 h. The reaction mixture was filtered through a sinter funnel, and the zinc residues washed with EtOAc (2 × 50 mL) and then methanol (50 mL). The combined filtrates were evaporated in vacuo and the residue purified by flash chromatography (5% methanol/EtOAc) to give the title product as a clear oil (0.37 g, 90%). − IR (liquid film): $\tilde{\nu}$ = 2970, 2877, 1702, 1645 cm^{-1}. − ^1H NMR (300 MHz, $CDCl_3$): δ = 1.66−2.00 (m, 3 H), 2.24 −2.38 (m, 1 H), 2.52 −2.70 (m, 6 H), 3.5−3.8 (m, 2 H), 3.94−4.06 (m, 1 H). − ^{13}C (75 MHz, $CDCl_3$): δ = 23.1 (CH_2), 32.0 (CH_2), 34.0 (CH_2), 39.0 (CH_2), 47.1 (CH_2), 50.4 (CH_2), 54.2 (CH), 171.8 (C=O), 207.4 (C=O). − LRMS: *m/z* = 167 [M^+], 98, 84, 70, 56. − HRMS: $C_9H_{13}NO_2$ M^+ calcd. 167.0946; found 167.0941.

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